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# SYNTHETIC ASPECTS OF ACYLSILANE CHEMISTRY

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Acylsilanes[1] show potential for becoming important synthetic intermediates. This overview of their chemistry[2] is not intended to be exhaustive, but is rather meant to delineate the principal preparative and reaction chemistry of these interesting species. Discussion of the latter is for the most part limited to those transformations which are unique to these ketones, or result in "unexpected" products as compared to asilyl ketone chemistry. Processes such as reduction,[3] derivatization to hydrazones,[4] and metalation to enolate anions,[5] for example, occur normally.

## I. Preparation of Acylsilanes

### A. Hydrolysis of α,α-Dibromobenzylsilanes

$$R_3SiCH_2Ar \xrightarrow{NBS} R_3SiCBr_2Ar \xrightarrow[HOH]{AgOAc} R_3SiCOAr$$

Acylsilane chemistry was initiated in 1957 with the report by Brook of the preparation of benzoyltriphenylsilane by this method.[6] This methodology demands site-specific dihalogenation and subsequent hydrolysis, requirements which place severe limitations on the approach, although a variety of substitution patterns on silicon[3b,7,8] and the aryl moiety[8] have been achieved. A recent report details a facile silica gel-promoted hydrolysis of the dibromo intermediates.[8d]

### B. Silyl-Metal Reagents plus Acyl Halides

$$R^1_3SiM + R^2C(O)X \rightarrow R^1_3SiC(O)R^2$$

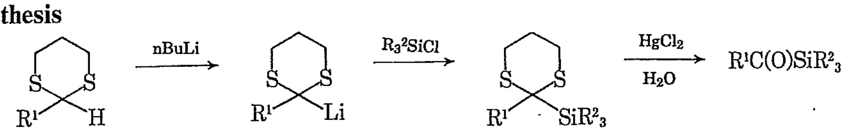
Original attempts to obtain acylsilanes by this method led to consistently low yields. Triphenylsilylpotassium and acetyl chloride afforded 4% of benzoyltriphenylsilane,[6] while similar results were obtained from triphenylsilyllithium and acetyl halides.[3b,9] However, more recent reports indicate that the addition of stoichiometric amounts of copper(I) halides to the silyllithium reagent prior to reaction with acyl halides leads to good yields of a number of acylsilanes.[10,11a] Interestingly, tris(trimethylsilyl)silyllithium and acid halides afford good yields of the resulting acylsilanes without the necessity of cuprous salts.[11]

### C. Oxidation of α-Silylcarbinols

$$R^1_3SiCH(OH)R^2 \xrightarrow{[O]} R^1_3SiC(O)R^2$$

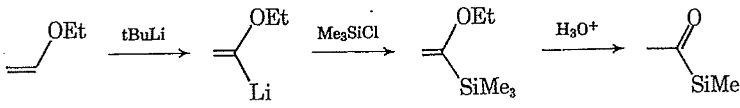
Although success in the oxidation of some α-silylcarbinols with Jones' Reagent has been reported,[2b,12] useful amounts of ketone could not be obtained from 1,1-diphenyl-sila-2-cyclohexanol under these conditions.[13] A more general procedure employs dicyclohexylcarbodiimide and pyridinium trifluoroacetate in dimethylsulfoxide.[3,11a,12,13] In the past, a major drawback to this overall process has been the relative unavailability of α-silylcarbinol precursors in synthetically useful amounts.

### D. Dithiane Synthesis



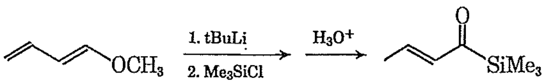
The use of lithiated dithianes as acyl anion equivalents[14] was applied to the synthesis of acylsilanes by several groups of workers simultaneously.[15] The scope of the method is quite large, with problems, if any, arising in the hydrolysis step. Phenyl-substituted intermediates ($R^1$ or $R^2$ = Ph, above) are slower to hydrolyze than alkyl counterparts, and the hydrolysis conditions appeared to lead to some decomposition of certain acyldisilanes ($R^1_3SiSiR^1_2COR^2$) or their precursor dithianes.[16] Nevertheless, this route remains attractive because of the flexibility afforded by metalating and then alkylating (silylating) dithiane itself in a stepwise fashion. The method has been applied to the synthesis of silacycloalkan-2-ones[17] and has also proven viable with bis(methylthio)methane in place of dithiane.[18]

### E. Silylation of (α-Alkoxyvinyl)metallic Reagents

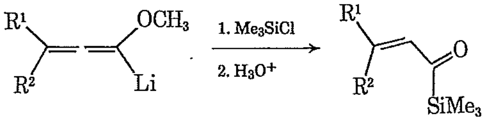


Following reports that alkyl vinyl ethers could be metalated to afford α-alkoxyvinyllithiums,[19] a route culminating in acylsilanes was developed by several groups.[20] Recently, a detailed study on the preparation of lithiated methyl vinyl ether and its use in the above context has appeared.[21] Although the method serves well for the preparation of acetylsilanes, some higher homologues may not be as readily accessible (1-methoxypropene can be α-metalated, but not β,β-disubstituted enol ethers[19b]). Moreover, with the exception of vinyl alkyl ethers, many alkenyl alkyl ethers are not readily available.

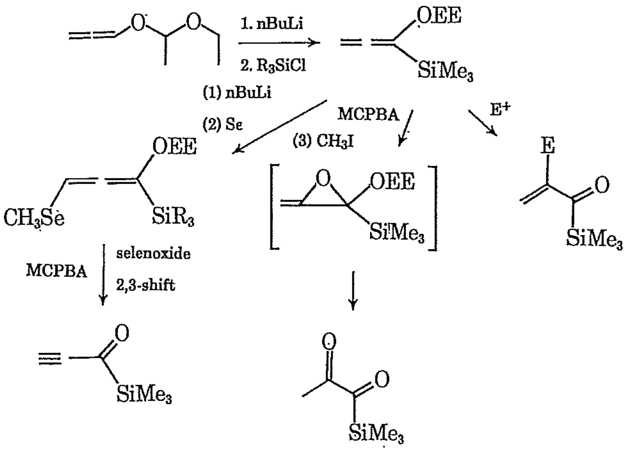
A variation on this approach involves the metalation of 1-alkoxy-1,3-butadienes[19b] to ultimately produce, after double bond isomerization, α,β-unsaturated acylsilanes.[22]



The more readily metalated allenyl alkyl ethers have also been shown to serve as α,β-unsaturated acylsilane precursors,[23] while a similar approach has served for the synthesis of cumulenyl silyl ketones.[24]

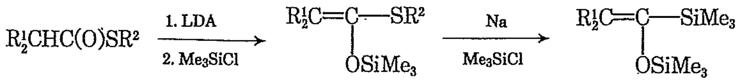


Imaginative extensions of this general methodology have recently been applied to the synthesis of conjugated alkenylacyl-, alkynylacyl-, and β-ketoacylsilanes.[25]



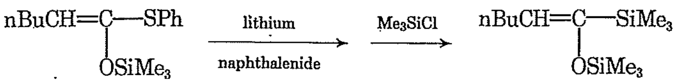
(E = H, Br, Cl, SePh)

A formally different approach to acylsilanes, yet one that is still based on the intermediacy of metalated alkenyl ethers, employs reductive metalation of monothio ketene acetals.[26] Thus, a mixture of sodium dispersion, the silyl enol ether of an S-methyl or S-phenyl ester and trimethylchlorosilane is refluxed in benzene to give high yields of the O-trimethylsilyl enol ether of an acyltrimethylsilane, readily hydrolyzed to the acylsilane itself.



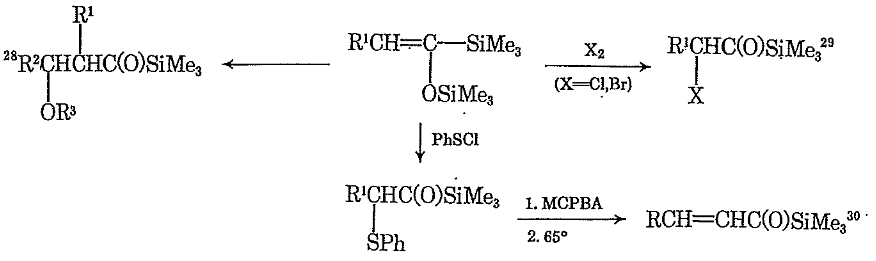
$$R^1_2CHC(O)SR^2 \xrightarrow[2.\ Me_3SiCl]{1.\ LDA} R^1_2C{=}\underset{OSiMe_3}{\underset{|}{C}}{-}SR^2 \xrightarrow[Me_3SiCl]{Na} R^1_2C{=}\underset{OSiMe_3}{\underset{|}{C}}{-}SiMe_3$$

Parallel chemistry with lithium as the counter ion to the presumed 1-alkoxyalkenyl anion has appeared.[27]



$$nBuCH{=}\underset{OSiMe_3}{\underset{|}{C}}{-}SPh \xrightarrow[naphthalenide]{lithium} \xrightarrow{Me_3SiCl} nBuCH{=}\underset{OSiMe_3}{\underset{|}{C}}{-}SiMe_3$$

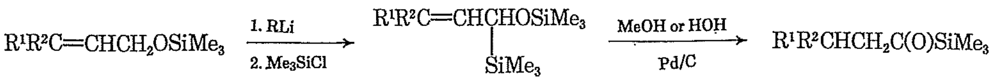
This availability of the silyl enol ethers of acylsilanes as primary reaction products has then led, by way of reaction with electrophiles, to a variety of functionalized acylsilanes.



$$^{28}R^2\underset{OR^3}{\underset{|}{C}}H\overset{R^1}{\overset{|}{C}}HC(O)SiMe_3 \longleftarrow R^1CH{=}\underset{OSiMe_3}{\underset{|}{C}}{-}SiMe_3 \xrightarrow[(X{=}Cl,Br)]{X_2} R^1\underset{X}{\underset{|}{C}}HC(O)SiMe_3{}^{29}$$

$$R^1CH{=}\underset{OSiMe_3}{\underset{|}{C}}{-}SiMe_3 \xrightarrow{PhSCl} R^1\underset{SPh}{\underset{|}{C}}HC(O)SiMe_3 \xrightarrow[2.\ 65^\circ]{1.\ MCPBA} RCH{=}CHC(O)SiMe_3{}^{30}$$

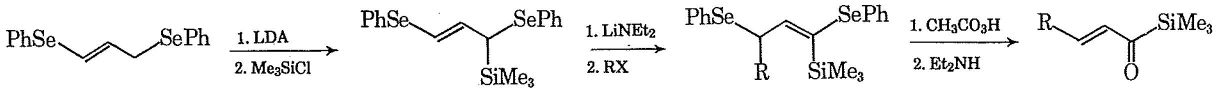
## F. Metalation/Silylation/Isomerization of Allyloxy and Propargyloxy Systems



$$R^1R^2C{=}CHCH_2OSiMe_3 \xrightarrow[2.\ Me_3SiCl]{1.\ RLi} R^1R^2C{=}CH\underset{SiMe_3}{\underset{|}{C}}HOSiMe_3 \xrightarrow[Pd/C]{MeOH\ or\ HOH} R^1R^2CHCH_2C(O)SiMe_3$$

Lithiation of allyloxysilanes affords an anion which, under proper conditions can be silylated to provide exclusively the $\alpha$-silyl isomer.[31] The application of this observation to the synthesis of acylsilanes rests on the demonstration that such silylated allyloxysilanes undergo sequential isomerization (to $\alpha$-silylalkenyl ethers) and hydrolysis upon treatment with palladium in protic solvents.[32]

A number of $\alpha,\beta$-unsaturated acylsilanes have been accessed by the sequence shown below, involving $\alpha$-silylallylselenyl species.[33]

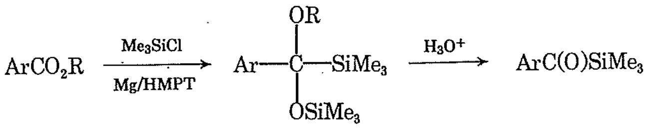


Deprotonation of propargyloxysilanes has been interpreted as initiating stepwise silyl group (1,2) and hydrogen (1,3) migrations culminating in a lithium allenoate which is hydrolyzable to the acylsilane shown.[34]

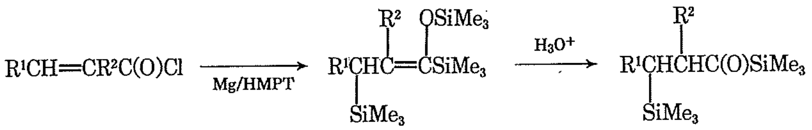
$$R^1{-}C{\equiv}CCH_2OSiR^2_3 \xrightarrow{\text{nBuLi}} R^1{-}C{\equiv}CCH(Li)OSiR^2_3 \longrightarrow R^1{-}C{\equiv}CCH(SiR^2_3)OLi \longrightarrow$$

$$\xrightarrow{H_3O^+} R^1CH{=}CHC(O)SiR^2$$

## G. Reductive Silylation of Carbonyl Compounds



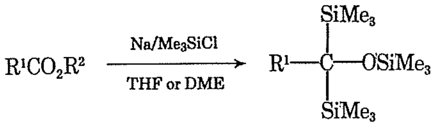
$$ArCO_2R \xrightarrow[\text{Mg/HMPT}]{Me_3SiCl} Ar{-}\underset{OSiMe_3}{\overset{OR}{C}}{-}SiMe_3 \xrightarrow{H_3O^+} ArC(O)SiMe_3$$



$$R^1CH{=}CR^2C(O)Cl \xrightarrow[\text{Mg/HMPT}]{} R^1\underset{SiMe_3}{C}H\overset{R^2}{C}{=}\overset{OSiMe_3}{C}SiMe_3 \xrightarrow{H_3O^+} R^1\underset{SiMe_3}{C}H\overset{R^2}{C}HC(O)SiMe_3$$

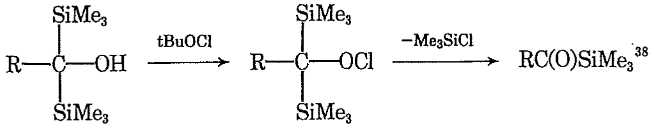
A series of reports beginning in 1969 described the behavior of a variety of carbonyl-containing compounds with the systems Mg-HMPT-$Me_3SiCl$[35] and Li-THF-$Me_3SiCl$.[36] The latter set of conditions and aliphatic esters afforded ketals or enoxysilanes which could be hydrolyzed to acylsilanes, but the method is plagued by production of mixtures and relatively low yields. The magnesium-HMPT process, employing aromatic carboxylic acid esters[35a,b,e] or $\alpha,\beta$-unsaturated carboxylic acid chlorides[35c] is more synthetically useful.

During the course of these studies, it had been noted that reductive silylation of certain esters with magnesium or lithium afforded the silyl ethers of 1,1-bis(trimethylsilyl)-1-alkanols.[35b,36] Other workers subsequently found that a wide variety of aliphatic esters afforded these products cleanly upon reductive silylation using sodium dispersion.[37]

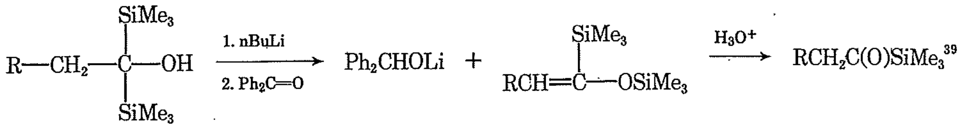


$$R^1CO_2R^2 \xrightarrow[\text{THF or DME}]{Na/Me_3SiCl} R^1{-}\underset{SiMe_3}{\overset{SiMe_3}{C}}{-}OSiMe_3$$

The alcohols arising from hydrolysis of these ethers are of interest in the present context because of their ability to be transformed into acylsilanes.

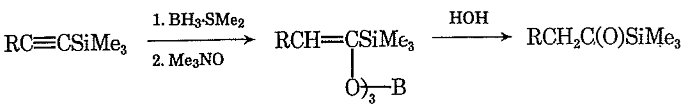


$$R{-}\underset{SiMe_3}{\overset{SiMe_3}{C}}{-}OH \xrightarrow{\text{tBuOCl}} R{-}\underset{SiMe_3}{\overset{SiMe_3}{C}}{-}OCl \xrightarrow{-Me_3SiCl} RC(O)SiMe_3{}^{38}$$



$$R{-}CH_2{-}\underset{SiMe_3}{\overset{SiMe_3}{C}}{-}OH \xrightarrow[2.\ Ph_2C{=}O]{1.\ \text{nBuLi}} Ph_2CHOLi + RCH{=}\overset{SiMe_3}{C}{-}OSiMe_3 \xrightarrow{H_3O^+} RCH_2C(O)SiMe_3{}^{39}$$

## H. Hydroboration-Oxidation of Silyl Acetylenes



$$RC{\equiv}CSiMe_3 \xrightarrow[2.\ Me_3NO]{1.\ BH_3{\cdot}SMe_2} RCH{=}\underset{(O)_3B}{C}SiMe_3 \xrightarrow{HOH} RCH_2C(O)SiMe_3$$

The first report on the hydroboration ($HBCl_2$)—oxidation ($Me_3NO{\cdot}2HOH$) of alkynylsilanes produced the desired acylsilanes in 25–35% overall yields.[40] An improved and more convenient adaptation of this procedure, however, was shown to provide a variety of acylsilanes in good to excellent yields.[41]

## I. Acid Chloride Cleavage of Disilanes

$$ArC(O)Cl + Me_3SiSiMe_3 \xrightarrow[P(OEt)_3]{[(\eta^3\text{-}C_3H_5)PdCl]_2} ArC(O)SiMe_3$$

Groups in both Japan[42a] and England[42b] have reported that benzoyl chloride reacts with hexamethyldisilane in the presence of palladium complexes as catalyst to form benzoyltrimethylsilane. The use of aliphatic acid chlorides results in much lower yields of acylsilanes.

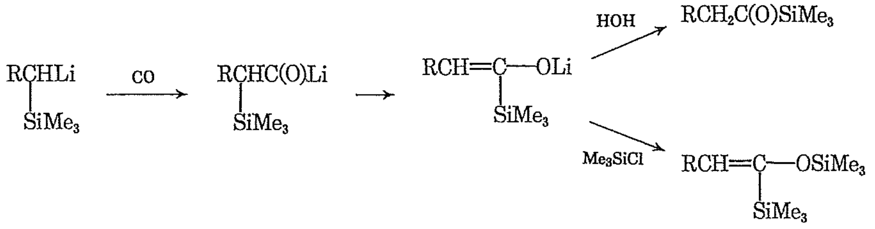
### J. Carbonylation-Silylation of Organolithium Reagents

$$RLi \xrightarrow[-110^\circ]{CO} RC(O)Li \xrightarrow{Me_3SiCl} RC(O)SiMe_3$$

The generation and *in situ* silylation of acyllithium intermediates have recently been described.[43] Although reaction conditions must be carefully controlled, good yields of acylsilanes can be obtained when R is a primary alkyl group. Complimentary chemistry, albeit by a distinctly different process, involves the reaction of phenyllithium with organosilylcobalttetracarbonyl complexes to afford benzoyltriphenylsilanes in moderate yields.[44]

$$Ph_3SiCo(CO)_4 \xrightarrow{PhLi} Ph_3SiC(O)Ph$$

One of the most promising methods in terms of generality, simplicity and yield for the synthesis of acylsilanes is represented by the sequence shown below. Carbonylation of $\alpha$-lithioalkylsilanes affords a presumed acyllithium species which rearranges (1,2 silyl group migration) to the enolate anion of an acylsilane.[45]



### K. Decarboxylation of Silyl $\alpha$-Ketoesters

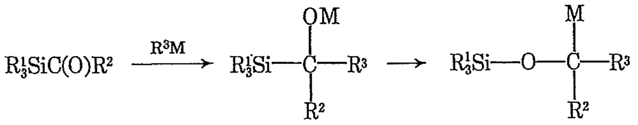
$$PhC(O)C(O)OSiMe_2Ph \xrightarrow{\Delta} PhC(O)SiMe_2Ph + CO_2$$

Benzoylsilanes can be prepared from the thermolysis of silyl $\alpha$-ketoesters.[46] With Ph = $CH_3$, a mixture of acylsilane and its thermal rearrangement product, the vinyloxysilane, is produced.

## II. Reactions of Acylsilanes

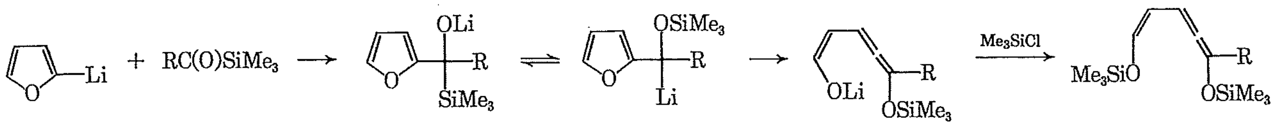
### A. With Organolithium and Grignard Reagents

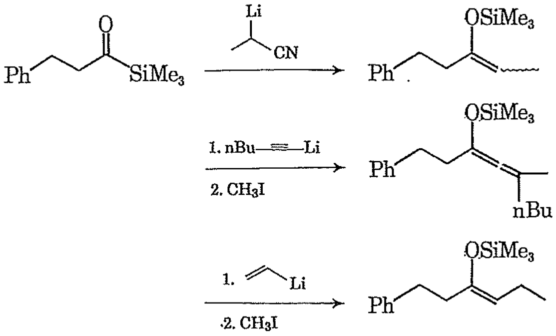
Benzoyltriphenylsilane adds methylmagnesium iodide to afford the expected 1-triphenylsilyl-1-phenylethanol,[47] but the use of alkyl Grignard reagents possessing a $\beta$-hydrogen leads to extensive reduction of the acylsilane to an $\alpha$-silylcarbinol.[3b] This is not a problem for Grignard reagents in which carbon bonded to magnesium is $sp^2$ or sp hybridized, and normal adducts may be obtained.[48] Nevertheless, associated with all additions of this type is the possibility that the initially formed oxyanionic intermediate will rearrange as shown.[2d,47,49]



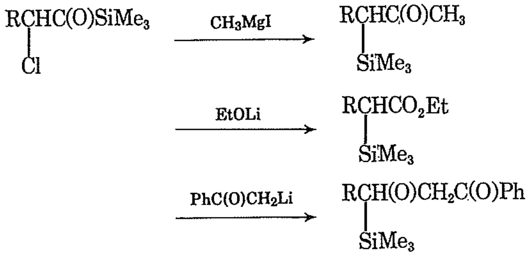
$$R^1_3SiC(O)R^2 \xrightarrow{R^3M} R^1_3Si-\underset{R^2}{\overset{OM}{C}}-R^3 \longrightarrow R^1_3Si-O-\underset{R^2}{\overset{M}{C}}-R^3$$

The rate of rearrangement is higher when $R^2$ and/or $R^3$ are capable of stabilizing the $\alpha$-metallo species, with lithium alkoxide intermediates rearranging faster than magnesium salts. Thus, except for the reaction of phenylmagnesium bromide with benzoyltriphenylsilane,[50] Grignard adducts of acylsilanes can be isolated as the carbinols, while organolithium adducts which can lead to stabilized carbanions by rearrangement generally do so *in situ*. Several research groups have initiated the exploitation of this phenomenon for the preparation of silyl enol ethers.[47a,51]



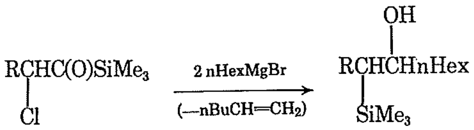


In contrast to the behavior of unfunctionalized acylsilanes, the reaction of α-haloacylsilanes with nucleophiles such as Grignard reagents,[52] alkoxides,[53] or enolate anions[54] results in silyl group migration to the *alpha*-carbon with concomitant loss of halide ion to form α-silylated carbonyl compounds.



$$\underset{\displaystyle Cl}{RCHC(O)SiMe_3} \xrightarrow{CH_3MgI} \underset{\displaystyle SiMe_3}{RCHC(O)CH_3}$$
$$\xrightarrow{EtOLi} \underset{\displaystyle SiMe_3}{RCHCO_2Et}$$
$$\xrightarrow{PhC(O)CH_2Li} \underset{\displaystyle SiMe_3}{RCH(O)CH_2C(O)Ph}$$

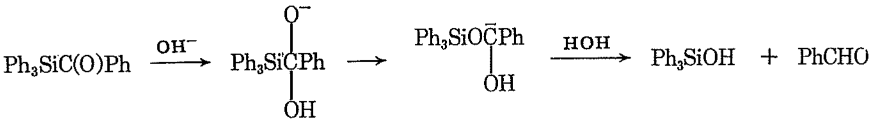
Grignard reagents with a β-hydrogen in the alkyl group act as hydride transfer agents.[52]



$$\underset{\displaystyle Cl}{RCHC(O)SiMe_3} \xrightarrow[(-nBuCH=CH_2)]{2\,nHexMgBr} \underset{\displaystyle SiMe_3}{RCH\overset{\displaystyle OH}{C}HnHex}$$

**B. With Hydroxide and Alkoxides**

One of the first observations concerning the reaction chemistry of acylsilanes was the fact that base effected the cleavage (protodesilylation) of the acyl-silicon bond,[6] apparently proceeding by way of the steps shown.[55]

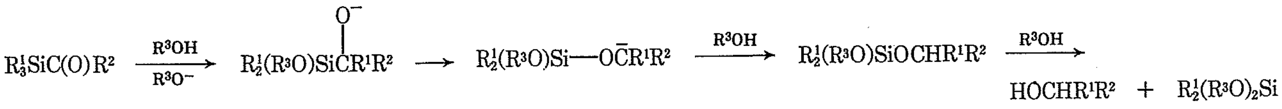


$$Ph_3SiC(O)Ph \xrightarrow{OH^-} Ph_3Si\underset{\displaystyle OH}{\overset{\displaystyle O^-}{C}}Ph \longrightarrow Ph_3SiO\underset{\displaystyle OH}{\bar{C}}Ph \xrightarrow{HOH} Ph_3SiOH + PhCHO$$

More recently, fluoride ion in the presence of proton donors or other electrophiles (alkyl halides, aldehydes, ketones) has shown similar results.[41b,56]

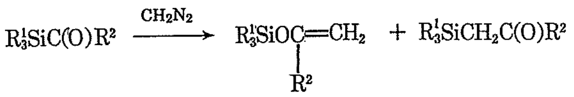
$$Me_3SiC(O)R \xrightarrow[EX]{F^-} RC(O)E$$

When acylsilanes are subjected to alkoxide/alcohol solutions, protodesilylation can be made minor, and migration of groups from silicon to carbonyl carbon occurs.[57]



$$R^1_3SiC(O)R^2 \xrightarrow[R^3O^-]{R^3OH} R^1_2(R^3O)Si\overset{\displaystyle O^-}{C}R^1R^2 \longrightarrow R^1_2(R^3O)Si{-}O\bar{C}R^1R^2 \xrightarrow{R^3OH} R^1_2(R^3O)SiOCHR^1R^2 \xrightarrow{R^3OH} HOCHR^1R^2 + R^1_2(R^3O)_2Si$$

**C. With Diazomethane and Alkylidenephosphoranes**



$$R^1_3SiC(O)R^2 \xrightarrow{CH_2N_2} R^1_3SiO\underset{\displaystyle R^2}{C}{=}CH_2 + R^1_3SiCH_2C(O)R^2$$

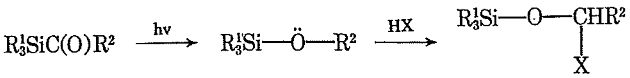
Mixtures of the indicated compounds are produced when $R^2$ = aryl, but the product is almost all ketone for $R^2 = CH_3$.[2b,58]

Methylenetriphenylphosphorane gives only silyl enol ether when $R^2$ = aryl, but the "normal" methylenated product (alkenylsilane) is the exclusive product when $R^2$ = alkyl.[59]

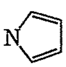
$$R^1_3SiC(O)R^2 \xrightarrow{CH_2=PPh_3} R^1_3SiO\underset{\displaystyle R^2}{C}{=}CH_2 + R^1_3Si\underset{\displaystyle R^2}{C}{=}CH_2$$

**D. Photolytic and Thermolytic Rearrangement**

Acylsilanes undergo ready photolysis upon absorption of light in the 330–440 nm region and appear to establish an equilibrium with a siloxycarbene. However, ensuing chemistry is highly co-reactant dependent. In the presence of alcohols and other materials capable of behaving as protonic acids, rearrangement of the acylsilane to a siloxy-carbene is followed by electrophilic trapping.[60]



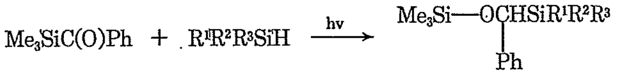
$$R^1_3SiC(O)R^2 \xrightarrow{hv} R^1_3Si{-}\ddot{O}{-}\ddot{C}{-}R^2 \xrightarrow{HX} R^1_3Si{-}O{-}\underset{\displaystyle X}{C}HR^2$$

[X = OH, OR, OAc, CN, Cl, , SPh, CH(CN)₂]

In chlorinated solvents, products arise which can be rationalized as stemming from a Norrish Type I cleavage of the acylsilane, although, depending on the solvent, other pathways are followed.[61]

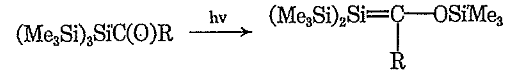
$$R^1_3SiC(O)R^2 \xrightarrow[hv]{CCl_4} R^1_3SiCl + R^2C(O)Cl + Cl_3CC(O)CH_3 + Cl_3CCCl_3$$

If solvent participation is curtailed by carrying out the photolysis in cyclohexane, a variety of products are formed which could arise through carbene or free radical processes.[5,62] Photolysis of acylsilanes in the presence of electron-poor olefins leads to cyclopropanes, while reaction with carbonyl-containing substrates affords oxiranes.[63] Benzoyltrimethylsilane has been shown to give products of apparent siloxycarbene insertion into the Si—H bond of mono- and diorganosilanes upon irradiation.[64]



$$Me_3SiC(O)Ph + R^1R^2R^3SiH \xrightarrow{hv} Me_3Si{-}OCH(Ph)SiR^1R^2R^3$$

The photolysis of acyldisilanes and, in particular, acyl(trissilyl)silanes, has recently been shown to generate compounds containing an example of a silicon-carbon double bond.[11,65] These are highly reactive species, but may be isolated when R is large.



$$(Me_3Si)_3SiC(O)R \xrightarrow{hv} (Me_3Si)_2Si{=}C(R){-}OSiMe_3$$

The thermolysis of a number of acylsilanes engenders transformations which again are best explained by postulating siloxycarbene participation[66]

$$Me_2CHC(O)SiMe_3 \xrightarrow{320°} Me_2C{=}CHOSiMe_3$$

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